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BARIUM TITANATE AND MANUFACTURE OF THE SAME

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[There are no amendments to this patent.]

Abstract

Objective

To offer a highly dispersive spherical barium titanate that allows control of particle diameter in accordance with the objectives.

Constitution

(1) Spherical barium titanate with a particle diameter of 0.2-5 μm, constituted by primary particles with particle diameters of 0.005-0.1 μm, formed by the addition of hydrogen peroxide in the manufacture of barium titanate by a hydrothermal reaction between a titanium compound and a barium compound.

(2) Cubic barium titanate or tetragonal barium titanate, produced by calcination of the resulting spherical barium titanate.

(3) A dense spherical barium titanate, produced by thermal reaction of the resulting spherical barium titanate under pressure.

Claims

1. Spherical barium titanate with a particle diameter of 0.2-5 μm, constituted by primary particles with particle diameters of 0.005-0.1 μm, where the particle diameter of the primary particles is 1/3 or less relative to the particle diameter of the spherical barium titanate.

2. Spherical barium titanate produced by calcination of the spherical barium titanate according to Claim 1.

3. Tetragonal barium titanate obtained by calcination of the spherical barium titanate according to Claim 1.

4. Spherical barium titanate obtained by hydrothermal reaction of the spherical barium titanate according to Claim 1 under pressurization.

5. Spherical barium titanate with a particle diameter of 0.2-5 μm, which internally contains particles with different particle diameters or particles with different compositions.

6. A method for manufacturing the spherical barium titanate according to Claim 1, characterized in that hydrogen peroxide is added along with a titanium compound and a barium compound, and a wet reaction is induced.

7. A method for manufacturing the spherical barium titanate according to Claim 6, characterized in that the titanium compound is titanium hydroxide or titanium oxide, the barium compound is barium hydroxide, and the titanium hydroxide or titanium oxide is mixed with the hydrogen peroxide, whereupon a wet reaction is allowed to occur with the barium hydroxide under normal pressure.

8. A method for manufacturing the spherical barium titanate according to Claim 7, wherein the concentration of the titanium compound is 0.01-2.5 mol/L by titanium oxide conversion, the molar ratio of barium is 0.8-10 with respect to titanium, the molar ratio of hydrogen peroxide is 0.1-10 with respect to the titanium compound, and the hydrothermal reaction temperature is 40-100°C.

9. The method for manufacturing spherical barium titanate according to Claim 7, characterized in that an aging reaction is carried out for 0.1 h or longer at a temperature between the temperature at which the reaction is completed in 4 h and a temperature that is 50°C below this temperature, whereupon a reaction is allowed to occur at no less than the temperature at which the reaction is completed in 4 h.

10. A method for manufacturing spherical barium titanate with a particle diameter of 0.2-5 μm, characterized in that the spherical barium titanate according to Claim 1 is allowed to undergo a hydrothermal reaction under pressurization.

11. A method for manufacturing orthogonal barium titanate, characterized in that the spherical barium titanate according to Claim 1 is adjusted so that the molar ratio of barium with respect to titanium is adjusted to 0.95-1.05, and calcination is carried out at 900-1300°C.

Detailed explanation of the invention

[0001]

Industrial application field

The present invention relates to barium titanate and a method for its manufacture.

[0002]

Prior art

Barium titanate is used as a dielectric material for electronic parts such as capacitors and PTC thermistors, but recently, highly dispersible barium titanate has come to be desired where the particle diameter of the barium titanate can be controlled in accordance with the objectives.

[0003]

Considering capacitors, for example, in order to obtain capacitors with good temperature characteristics in high dielectric constant systems, niobium and cobalt are added to tetragonal barium titanate, and the crystal structure of the tetragonal barium titanate is thus changed from the ceramic grain boundary towards the interior, thus producing a so-called core-shell sintered body. However, in order to obtain a material with good characteristics, it is necessary for the particle diameter of the ceramic to be 0.5-1 μm, and for the particle diameters to be uniform. In obtaining

this type of ceramic, the barium titanate that serves as the raw material must have a particle diameter of 0.5-1 μm, and should also have a narrow particle size distribution.

[0004]

In addition, with laminated capacitors constituted by systems with high dielectric constants, the dielectric ceramic layers are thin. Although this increases capacitance and reduces the size of the capacitor, it is necessary for the particle diameter to be 0.2-1 μm with a narrow particle size distribution in order to obtain ceramic layers with good withstand voltage characteristics. It is also necessary for the barium titanate to have good dispersibility.

[0005]

Moreover, semiconductor capacitors and PTC thermistors having positive temperature characteristics are devices that employ the electrical characteristics of the ceramic grain boundary, but it is thought that materials having good characteristics in this regard have uniform grain boundary layer thicknesses and uniform particle diameters. Consequently, with these devices as well, it is necessary for the raw material barium titanate to have a particle diameter of 1-5 μm, and for the particle size distribution to be narrow, if products with favorable characteristics are to be produced.

[0006]

However, barium titanates manufactured by past methods have not adequately responded to the above demands.

[0007]

Specifically, in the conventional manufacture of barium titanate, the barium titanate has been manufactured by carrying out a solid-phase reaction involving mixed calcination of a titanium compound and a barium compound. With this type of solid-phase reaction, however, the particle diameter of the resulting barium titanate is large because the reaction is carried out at high temperatures, and even if mechanical pulverization is carried out, the particle diameter will not be reduced, and the particle size distribution will widen. For this reason, it has not been possible to control the particle diameter, and nonuniform shapes have been produced, resulting in poor particle dispersion and a material that is completely unable to satisfy the above demands.

[0008]

Thus, in order to solve the above problems, manufacture of barium titanate by a wet method has been proposed. For example, a manufacturing method for barium titanate has been

offered in Japanese Kokai Patent Application No. Sho 61[1986]-31345 which involves the use of a hydrothermal method or alkoxide method.

[0009]

However, these methods only allow the production of barium titanate having a fine particle diameter, and moreover, the particle shapes are distorted, leading to the disadvantage that the resulting material has aggregated particles. Consequently, these methods also do not allow the production of barium titanate having good dispersibility, while allowing control of the particle diameter at a target particle diameter in the range of 0.2-5 μm.

[0010]

In addition, although barium titanate used in the production of core-shell sintered bodies must be orthogonal, when orthogonal barium titanate obtained by dry-phase methods is calcined, and in addition, when orthogonal barium titanate is produced by the calcination of pseudo-cubic barium titanate obtained by wet methods, the growth of the particles proceeds nonuniformly, so that sintering between particles is extreme. As a result, the particle size distribution widens, and these materials are thus completely unable to respond to the above demands.

[0011]

Problems to be solved by the invention

As described above, conventional barium titanates do not allow sufficient control of particle diameters, and in addition, have poor dispersibility. Consequently, these materials have had problems responding sufficiently well to demands regarding size reduction and performance increase in electronic parts such as capacitors and PTC thermistors.

[0012]

The present invention thus has the objective of offering a barium titanate that is highly dispersible and allows control of its particle diameter in accordance with the objectives.

[0013]

Means to solve the problems

The inventors of the present invention, et al., as a result of repeated investigations on various fronts concerning the control of particle size and particle shape of barium titanate, arrived at the present invention upon discovering that the use of hydrogen peroxide to manufacture barium titanate in a wet reaction between a titanium compound and a barium compound allows the

production of a spherical barium titanate, and that this method affords control of the particle diameter as desired, thereby fully achieving the above objectives.

[0014]

Specifically, the barium titanate of the present invention is a spherical barium titanate with a particle diameter of 0.2-5 μm having a narrow particle size distribution, which is produced by the firm aggregation and bonding, into spheres, of primary particles of fine barium titanate having particle diameters of 0.005-0.1 μm. This spherical barium titanate is obtained by a wet reaction between a barium compound and a titanium compound, using hydrogen peroxide.

[0015]

In the wet reaction between the aforementioned titanium compound and barium compound, the hydrogen peroxide causes a slow progression of the barium titanate formation reaction, and this is thought to cause the production of spherical barium titanate with a particle diameter of 0.2-5 μm having a narrow particle size distribution, where barium titanate primary particles having particle diameters of 0.005-0.1 μm are aggregated into spheres.

[0016]

Thus, the spherical barium titanate is thought to form by a type of chemical bonding, in addition to the simple physical aggregation of primary particles of barium titanate. As a result, the barium titanate consists of firmly aggregated and bound primary particles of barium titanate, and will not break down in handling processes used in the manufacture of electronic parts such as capacitors or PTC thermistors.

[0017]

By varying the reaction conditions of the wet reaction and other parameters, it is possible to freely control the particle diameter of the barium titanate that is obtained.

[0018]

The spherical barium titanate obtained in this manner can be used without modification as a raw material for the production of electronic parts such as capacitors and PTC thermistors. In other words, the material can be used as a raw material for electroceramics. However, by calcination of this material in order to convert the crystal structure into a cubic crystal or tetragonal crystal, control of the ceramic particle form and grain boundary is facilitated, and a more desirable electroceramic raw material can be obtained.

[0019]

Specifically, the aforementioned spherical barium titanate is converted from a pseudo-cubic crystal morphology to a cubic or tetragonal crystal morphology by means of calcination at 600°C or greater, thus improving crystallinity and facilitating greater control of the particle diameter or grain boundary of the ceramic as described above. However, when forming the cubic or tetragonal barium titanate, the spherical barium titanate is literally spherical prior to calcination, and there are few interparticle contact points, so that little sintering occurs during calcination. The particle size of the spherical barium titanate prior to calcination is thus fairly well maintained, resulting in a narrow particle size distribution and excellent dispersibility.

[0020]

Moreover, when the aforementioned spherical barium titanate is allowed to react again under pressurization (hydrothermal reaction), a more dense spherical barium titanate can be obtained which produces a material that facilitates greater control of the ceramic particle diameter and grain boundary.

[0021]

Moreover, when manufacturing spherical barium titanate in the present invention, particles of barium titanate are formed which have particle diameters that are smaller than the particle diameter of the resulting spherical barium titanate, along with particles of other perovskite-form compounds. Consequently, a spherical barium titanate can be obtained which contains particles with different particle diameters and particles with different compositions.

[0022]

The particles of different particle diameter or composition contained inside the spherical barium titanate of this type improve the ceramic electrical characteristics, and also aid in improving crystallinity of the particles resulting from firing or calcination. As a result, these particles bring about additional improvement in the spherical barium titanate characteristics.

[0023]

Next, details will be presented regarding the reaction raw materials and reaction methods used in producing the spherical barium titanate of the present invention.

[0024]

Reaction raw materials

In the present invention, a titanate compound and barium compound are used as reaction raw materials, and hydrogen peroxide is used during the reaction. The explanation presented below is based on addition of the materials in the order: titanium compound, barium compound, hydrogen peroxide.

[0025]

There are no particular restrictions on the titanium compound, provided that it can generate perovskite-form barium titanate together with the barium compound. However, it is preferable to use a material that partially or completely dissolves in aqueous hydrogen peroxide solution. In addition, a material is also preferred which contains a minimum amount of content that compromises the physical properties of the resulting barium titanate by admixture therein.

[0026]

In light of the above considerations, examples of preferred titanium compounds that may be cited include titanium oxide, titanium hydroxide and other inorganic titanium compounds, and titanium oxalate, titanium alkoxide and other organic titanium compounds.

[0027]

Titanium oxide and titanium hydroxide which are easy to obtain on an industrial scale are often used. When using titanium hydroxide, it is preferable to measure the ignition loss in order to calculate the weight of the titanium oxide (TiO_2) in the titanium hydroxide, and to use this titanium oxide weight as a standard for the weight ratio used in the wet reaction with the barium compound. In measurement of the ignition loss, it is appropriate to use the standard of heating for 2 h at 1000°C.

[0028]

There are no particular restrictions on compounds that are used for the barium compound, provided they can form perovskite-form barium titanate by reacting with the aforementioned titanium compound. However, it is generally preferable to use basic barium compounds.

[0029]

It is also preferable to use a material containing minimal amounts of components that will compromise the characteristics of the barium titanate by admixture therein. In light of these

considerations, examples of preferred barium compounds that may be cited include barium hydroxide, barium oxide and barium alkoxide.

[0030]

There are no particular restrictions on the hydrogen peroxide, and various materials may be used. However, from the standpoint of ease of handling and procurement, it is generally preferable to use commercial 30% (wt%, likewise below) aqueous hydrogen peroxide aqueous solution, 35% aqueous hydrogen peroxide solution, 50% aqueous hydrogen peroxide solution or 60% aqueous hydrogen peroxide solution.

[0031]

Reaction methods

There are no particular restrictions on the order of addition of the titanium compound, barium compound and hydrogen peroxide, but in order to exclude reactions under dilute concentrations, it is preferable to mix the titanium compound and hydrogen peroxide prior to the addition of the barium compound, and then to mix the materials to bring about the reaction. If, in order to exclude reactions under dilute concentrations, the hydrogen peroxide is added to a system in which the barium compound is present, poorly-soluble barium oxide (BaO_2) will precipitate, and will be unavailable for use in the reaction.

[0032]

The hydrogen peroxide is preferably used at a H_2O_2/TiO_2 ratio of 0.1-10 (molar ratio) in terms of the ratio of hydrogen peroxide with respect to titanium compound (specifically, titanium oxide conversion).

[0033]

If the amount of hydrogen peroxide exceeds a molar ratio of 10 with respect to the above titanium compound, decomposition will occur at the time of reaction with the titanium compound, and such amounts are thus not economical. In addition, if the amount of hydrogen peroxide is less than a molar ratio of 0.1 with respect to the aforementioned titanium compound, sufficient effects will not be produced due to the addition of the hydrogen peroxide.

[0034]

When mixing the titanium compound and hydrogen peroxide, titanium peroxide is commonly generated in the reaction, and the color turns yellow. Upon completion of the reaction,

a completely dissolved aqueous titanium peroxide solution can be used, or a suspension containing the generated titanium peroxide can also be used.

[0035]

For example, when the titanium oxide conversion concentration in the titanium hydroxide slurry is low, at 0.05-0.25 mol/L, a completely dissolved aqueous titanium oxide solution will be produced by mixing hydrogen peroxide in an amount that is 3x or greater with respect to the titanium in terms of molar ratio.

[0036]

However, if the titanium oxide conversion concentration in the titanium hydroxide slurry is high, at 1 mol/L, or if crystalline titanium oxide is used, a completely dissolved aqueous solution will not be obtained regardless of the concentration and regardless of the amount of hydrogen peroxide. A suspension solution will thus result. In other words, manufacture of spherical barium titanate will not be impaired, regardless of whether the material is the aforementioned type of titanium peroxide as a completely dissolved aqueous solution or the suspension solution.

[0037]

Ordinary temperatures can be used during mixing of the hydrogen peroxide, but it is preferable to heat the reaction to 40-100°C in order to obtain a completely dissolved aqueous solution or a dispersion with uniform titanium peroxide content in a comparatively short period of time.

[0038]

It is desirable for the titanium oxide conversion concentration of the titanium compound, after addition of the barium compound, to be 0.01-2.5 mol/L, with 0.06-1 mol/L being preferred. If the above concentration exceeds 2.5 mol/L, then a condition will result in which stirring is difficult due to high viscosity, and the barium titanate obtained by the reaction with the barium compound will not have a uniform particle diameter. If the above concentration is less than 0.01 mol/L, on the other hand, the reactivity will be dramatically reduced.

[0039]

In addition, additives that may be used for improving characteristics or as sintering aids when electroceramic formation is to be performed include 0.01-10% of trace metals, nonmetallic substances, or compounds thereof, which may be added prior to the reaction with the barium compound.

[0040]

The barium compound is added and mixed until uniform to bring about a reaction so that the molar ratio of barium with respect to titanium in the completely dissolved aqueous solution or the suspension solution of titanium peroxide obtained in this manner, or in other words, the Ba/Ti ratio (molar ratio), is 0.8-10, with 1-3 being preferred.

[0041]

At this time, pseudo-cubic perovskite-form barium titanate is formed by a reaction between the titanium compound and barium compound, but in order to obtain spherical barium titanate with a secondary particle diameter of 0.2-5 μm and a primary particle diameter of 0.005-0.1 μm, it is preferable for the titanium and barium molar ratio, barium compound concentration, reaction temperature and other parameters to be set so that the barium titanate generation reaction is completed within 1 h, and preferably within 4 h.

[0042]

Thus, in order to produce a spherical barium titanate with a uniform particle diameter and narrow particle size distribution, it is preferable for mixing of the titanium compound and barium compound to be performed at a temperature that is no greater than the initiation temperature of the reaction.

[0043]

Moreover, it is preferable to also carry out an aging reaction for at least 0.1 h, with 1 h or longer being preferred, at a temperature that is between the temperature that allows completion of the reaction between the aforementioned titanium compound and barium compound within 4 h and a temperature that is 50°C lower than this temperature, and preferably, between a temperature that allows the reaction to be completed within 4 h and a temperature that is 40°C below this temperature. Upon completion of the aging reaction, it is preferable for the reaction to be completed by allowing a reaction to occur at a temperature that is no less than the temperature that completes the reaction in 4 h. Completion of the aforementioned reaction refers to a condition in which further reaction produces no substantial change in the barium titanate integrated intensity determined by X-ray diffraction.

[0044]

Ordinarily, the aging reaction is carried out at 40-100°C, with 60-100°C being preferred. This aging reaction is carried out under normal pressure or reduced pressure. When this aging

reaction is carried out, for example, under pressurization conditions using a sealed vessel, the resulting barium titanate will tend to have fine particles of 0.1 μm or less, and in addition, even if particles of size 0.2 μm or greater are formed, nonspherical particles will be included, and the particle size distribution will increase, making it impossible to obtain the 0.2-5-μm spherical barium titanate of the present invention. This trend becomes pronounced when the reaction is carried out at 100°C or greater under pressurization.

[0045]

During the reaction, it is preferable for nitrogen to be introduced into the reaction system so that components in air such as carbon dioxide gas do not react with the barium compound.

[0046]

As described above, a spherical barium titanate with a particle diameter of 0.2-5 μm composed of primary particles with particle diameters of 0.005-0.1 μm is obtained, but in the present invention, it is a necessary condition that, regarding the relationship between the primary particle diameter and the secondary spherical barium titanate particle diameter, the particle diameter of the primary particles is 1/3 or less of the particle diameter of the [secondary] spherical barium titanate. This condition is used because if the particle diameter of the primary particles is greater than 1/3 of the particle diameter of the spherical barium titanate secondary particles, then the sphericity will be compromised, and a spherical barium titanate with good dispersibility will not be obtained. In particular, it is preferable for the particle diameter of the primary particles to be 1/5 or less the particle diameter of the spherical barium titanate.

[0047]

In the present invention, the particle diameter of the spherical barium titanate is specified at 0.2-5 μm, and the reasons for this are presented below. Specifically, if the particle diameter is less than 0.2 μm, the dispersibility will be poor. For example, dispersibility in the binder will be poor during formation prior to producing a ceramic, making it difficult to obtain uniform moldings. In addition, if the particle diameter is greater than 5 μm, it will not be possible to use the material to produce increasingly thin and small-sized electronic ceramic parts such as capacitors and PTC thermistors.

[0048]

In addition, it is a necessary condition that the particle diameter of the primary particles be 0.005-0.1 μm. The reason for this requirement, to be brief, is that a material with a primary particle diameter of less than 0.005 μm cannot be obtained by wet methods. On the other hand, if the

primary particle diameter is greater than 0.1 μm, the temperature used for carrying out firing or calcining will increase, and it will be difficult to obtain a barium titanate with good dispersibility and minimal sintering.

[0049]

Next, factors that allow control of the barium titanate particle diameter or particle form will be discussed in detail using actual examples. In this example, a titanium hydroxide cake obtained by hydrolysis of aqueous titanium tetrachloride solution using aqueous ammonia solution is employed, and a slurry is produced having a titanium oxide concentration of 0.312 mol/L. Hydrogen peroxide is then added and mixed in this slurry at a H_2O_2/TiO_2 ratio (molar ratio) of 6.35, and a suspension solution is obtained by stirring for 2 h at 60°C.

[0050]

The temperature of this aqueous solution is then decreased to 40°C, and barium hydroxide·octahydrate is added and mixed with this aqueous solution to produce a Ba/Ti (molar ratio) of 1.4. After mixing, an aging reaction is allowed to occur for 2 h at 70°C while stirring, and subsequently, spherical barium titanate with an average particle diameter of 1 μm is obtained by a 4-h reaction at 100°C.

[0051]

First, the effect of the solution concentration on the particle diameter and particle form of the barium titanate particles will be discussed in reference to the above reaction example.

[0052]

The particle diameter tends to decrease as the concentration of the solution, particularly the barium ion concentration, increases.

[0053]

In this reaction example, if the Ba/Ti (molar ratio) is held constant at 1.4 and the titanium oxide conversion concentration in the solution becomes higher than 0.312 mol/L, then the barium ion concentration will increase. As a result, the particle diameter of the barium titanate will be smaller than the 1 μm in the above reaction example. Conversely, if the titanium oxide conversion concentration is low, at less than 0.312 mol/L, then the barium ion concentration will decrease, and the particle diameter will be greater than 1 μm.

[0054]

In addition, with regard to the temperature of the reaction between the titanium compound and hydrogen peroxide, the particle diameter of the barium titanate decreases as the temperature increases, and the particle diameter of the barium titanate increases as the temperature decreases.

[0055]

In particular, although a completely dissolved aqueous solution or a suspension of the titanium oxide is produced by mixing the titanium compound slurry and hydrogen peroxide, the solution is aged at 20-100°C, at this time, after mixing the titanium compound slurry and the hydrogen peroxide. As the aging temperature increases, the particle diameter decreases, and as the aging temperature decreases, the particle diameter increases.

[0056]

Regarding the Ba/Ti ratio (molar ratio), the barium ion concentration increases as this ratio increases, and the particle diameter of the barium titanate tends to decrease.

[0057]

In the aforementioned reaction example, the amount of barium compound was adjusted so that the Ba/Ti ratio (molar ratio) was 1.4, but if this ratio is greater, the barium ion concentration will increase, and the reaction rate will increase, leading to a decrease in particle diameter, although the particle form will not change. However, if the Ba/Ti ratio (molar ratio) is greater than 10, and the reaction is carried out under an extremely large excess of barium ions, the barium titanate will no longer aggregate, and fine particles will be produced.

[0058]

If the amount of barium hydroxide is so small as to produce a Ba/Ti ratio (molar ratio) that is less than 1.4, then the barium ion concentration will decrease, and the particle diameter will increase, although the particle form will not change. However, if the reaction is carried out under a Ba ion concentration that is so small that the Ba/Ti ratio (molar ratio) is less than 0.8, then the reaction itself will not occur.

[0059]

However, it will be possible to produce spherical barium titanate if the Ba/Ti ratio (molar ratio) is less than 0.8 at a certain point, but by the end of the reaction, the Ba/Ti ratio (molar ratio) has increased to 0.8 or greater.

[0060]

Next, the influence of the temperature of the aging reaction on particle diameter will be discussed. The particle diameter will increase to the extent that a lengthy aging reaction is carried out at a temperature that is near the temperature at which the barium titanate is produced. In addition, the particle diameter decreases as this aging temperature increases.

[0061]

For example, when the aging reaction is carried out at a temperature that is lower than 70°C, for example, a temperature at which the reaction rate is dramatically reduced, e.g., an aging reaction for 2 h at 50°C, if the temperature is subsequently increased to 100°C, the resulting barium titanate will be spherical with an average particle diameter of 0.6 μm, similar to the barium titanate obtained by an aging reaction at 100°C obtained by increasing the temperature as rapidly as possible from 20°C to 100°C. Specifically, the same results will occur whether the aging reaction is carried out at a low temperature that does not accelerate the reaction or not, and thus such a reaction has no significance.

[0062]

When an aging reaction is carried out at a temperature that is higher than 70°C, the reaction rate will increase, and the particle diameter will decrease, although the particle form will not change. For example, if a sealed container is used and the aging temperature is increased to about 180°C, the reaction rate will be too fast, and a particle form produced by the formation of aggregates will not be maintained, so that all of the resulting barium titanate will be microparticles.

[0063]

In addition, if the aging temperature is decreased relative to the above reaction example, and the aging time is also increased so that an aging reaction is carried out while increasing the temperature from 60°C to 70°C over the course of 10 h, followed by a 4-h reaction at 100°C, then the particle diameter of the resulting barium titanate will be larger than in the aforementioned reaction example, producing an average particle diameter of 2.5 μm.

[0064]

By using the above types of reaction raw materials and reaction methods, a spherical barium titanate with a narrow particle size distribution of 0.2-5 μm, constituted by primary particles with particle diameters of 0.005-0.1 μm, will be obtained.

[0065]

The resulting spherical barium titanate is ordinarily subjected to a water wash and acid wash, and is used after adjusting the Ba/Ti ratio (molar ratio) to 0.95-1.05, with 0.99-1.02 being preferred.

[0066]

The aforementioned spherical barium titanate has a spherical form, and thus has superior dispersion properties. In addition, by selecting the aging reaction temperature, titanium compound concentration and Ba/Ti ratio (molar ratio), among other factors, it is possible to control the particle diameter as desired. Consequently, the material can be adjusted to a particle diameter in accordance with objectives, which contributes to size reduction and performance enhancement in electronic parts such as capacitors and PTC thermistors. Moreover, the material can respond sufficiently to demands regarding high dispersibility.

[0067]

Next, in the section titled: "Cubic barium titanate and tetragonal barium titanate obtained by calcination," a description will be presented regarding a 0.2-5-μm spherical barium titanate constituted by the aforementioned primary particles with particle diameters of 0.005-0.1 μm. In the section titled "Dense spherical barium titanate obtained by additional reaction under pressurization," and in the section titled "Spherical barium titanate containing particles of different particle form and composition" carried out utilizing the present invention, a spherical barium titanate with a particle diameter of 0.2-5 μm is described, which is constituted by primary particles having particle diameters of 0.005-0.1 μm.

[0068]

Cubic barium titanate and tetragonal barium titanate obtained by calcination

The spherical barium titanate obtained in the present invention can be used as-is as a raw material for electroceramics, but the material is in a state in which primary particles are aggregated, and the crystal form is pseudo-cubic.

[0069]

Thus, when this material is calcined at 600°C or greater, the crystal form converts to a cubic or tetragonal form and the binding properties improve, thus producing a barium titanate that affords easier control of ceramic particle diameter and grain boundary.

[0070]

For example, when the spherical barium titanate is calcined at 600-1100°C, a cubic or tetragonal spherical barium titanate is obtained which has good dispersibility and minimal sintering, wherein the particle diameter and particle form of the spherical barium titanate have been maintained.

[0071]

In addition, when the material is calcined at 900-1300°C, a cubic barium titanate is obtained. In this case, if the temperature is low and the particle diameter is large, then the form will be more spherical. If the particle diameter is small and sintering is performed at high temperature, on the other hand, then a rectangular parallelepipedal single-crystal powder will be produced.

[0072]

By means of calcining as described above, a barium titanate that is highly dense and has good crystallinity will be obtained. In addition, regarding use in the formation of ceramics, the material will provide an electroceramic raw material that facilitates better control of the particle diameter and grain boundary.

[0073]

With cubic barium titanate and tetragonal barium titanate, the form of the spherical barium titanate prior to calcining will be literally spherical, and because there are few contact points between particles, there will be little sintering during calcining. As a result, the precalcining particle diameter will be well maintained, resulting in a narrow particle size distribution and superior dispersibility.

[0074]

Thus, with the cubic barium titanate and tetragonal barium titanate, it will be possible to control the particle diameter in accordance with the objectives based on the precalcining characteristics of the spherical barium titanate. In addition, the characteristic of high dispersibility will be maintained, and the utility of the material will be high relative to materials produced by calcining barium titanate obtained by conventional wet methods.

[0075]

Dense spherical barium titanate obtained by additional reaction under pressurization

The 0.2-5-μm spherical barium titanate constituted by primary particles with particle diameters of 0.005-0.1 μm of the present invention can be subjected to additional reaction under pressurization (hydrothermal reaction) in order to obtain a denser spherical barium titanate.

[0076]

This hydrothermal reaction that is carried out under reduced pressure can be performed on isolated spherical barium titanate, or can be performed without isolation in a process that is continuous with manufacture of the spherical barium titanate under normal pressure.

[0077]

Addition of barium compound during the hydrothermal reaction carried out under pressurization has the action of stimulating growth of primary particles, so that the spherical barium titanate with larger primary particles produced in this manner will provide a raw material that facilitates the production of ceramics having additives distributed at the grain boundary.

[0078]

The barium titanate obtained by a hydrothermal reaction carried out under pressurization in this manner can be used without modification, or may be used after calcining to produce a calcined powder.

[0079]

The spherical barium titanate obtained by the hydrothermal reaction carried out under pressurization in the manner described above is denser, allowing greater control of the ceramic particle diameter and grain boundary. As a result, the density of the ceramic is increased, withstand voltage is increased, and improvements in mechanical characteristics can be more readily achieved.

[0080]

Spherical barium titanate containing particles of different particle diameter or different composition

In addition, by employing the method of the present invention, it is possible to manufacture a spherical barium titanate that internally contains particles having a different particle diameter or composition.

[0081]

For example, it is possible to manufacture a spherical barium titanate that internally contains tetragonal barium titanate particles having a different particle diameter by using tetragonal barium titanate with good crystallinity and a particle diameter that is smaller than the intended particle diameter of 0.1 μm or greater, and employing the method of the present invention with this tetragonal barium titanate as crystallization nuclei. Thus, by calcining spherical barium titanate internally containing tetragonal barium titanate, a tetragonal cuboid barium titanate can be more readily obtained.

[0082]

In addition, the method of the present invention can also be carried out by using, as crystallization nuclei, strontium titanate, barium zirconate, barium titanate zirconate or other perovskite compounds having high-temperature sintering properties with particle diameters that are smaller than that of the intended particles to be generated, where these compounds contribute to improving electrical characteristics of devices such as capacitors and PTC thermistors. By this means, it is possible to manufacture a spherical barium titanate that internally contains particles of different composition such as strontium titanate, barium zirconate or barium titanate zirconate.

[0083]

By means of firing the spherical barium titanate that internally contains particles of different composition, it is possible to carry out low-temperature sintering while allowing the barium titanate and particles of different composition used as crystallization nuclei to react. It is thus possible to improve the electrical characteristics of the barium titanate through low-temperature sintering using particles of different composition that sinter at high temperatures.

[0084]

The spherical barium titanate that internally contains these particles of different particle diameter or composition can be obtained by using particles of different diameter or different composition having good crystallinity obtained by solid-phase methods, or particles having different diameters or compositions with good crystallinity obtained by calcining particles obtained by wet methods. These particles are added and mixed with titanium alkoxide or titanium salt aqueous solution, or with titanium hydroxide or titanium oxide obtained by the hydrolysis of these materials, followed by the addition and mixing of hydrogen peroxide and a barium compound to bring about a reaction.

[0085]

The spherical barium titanate containing particles of different particle diameter or composition obtained by utilizing the method of the present invention in this manner has a narrow particle size distribution and good dispersibility, which are both characteristics of the spherical barium titanate of the present invention.

[0086]

In manufacturing the aforementioned spherical barium titanate internally containing particles or different particle diameter or composition, the hydrogen peroxide may be added directly to the aqueous solution of titanium alkoxide or titanium salt, or the hydrogen peroxide can be added after hydrolysis. Specifically, the hydrogen peroxide can be added and mixed at any stage prior to mixing and reacting of the barium compound.

[0087]

Mixing of the particles of different particle diameter or composition is preferably carried out prior to hydrolysis of the titanium alkoxide or titanium salt aqueous solution. This is because the titanium hydroxide will deposit onto the particle surfaces due to hydrolysis if the material has been added prior to hydrolysis, and the titanium hydroxide will then react with the barium compound so that the particles having different particle diameters or composition will be properly enclosed on the interior of the barium titanate. In addition, it is preferable for the particles of different particle diameter or composition to be well dispersed in the wet system prior to mixing.

[0088]

In the manufacture of the spherical barium titanate containing the above tetragonal barium titanate, there are no particular restrictions on the tetragonal barium titanate that is used, but it is preferable to use a material with a narrow particle size distribution obtained by a firing method or autoclave method, or a tetragonal cuboid barium titanate obtained by the calcination of the spherical barium titanate of the present invention.

[0089]

Effect of the invention

The spherical barium titanate of the present invention allows control of particle diameter in accordance with objectives, and in addition, has superior dispersibility due to its spherical form.

[0090]

Consequently, the spherical barium titanate of the present invention can respond sufficiently well to the desire for high dispersibility with control of particle diameter in accordance with objectives. Increasingly, these qualities have been in demand for barium titanate as size has decreased and performance has increased in electrical parts such as capacitors, PTC thermistors and piezoelectric bodies.

[0091]

The spherical barium titanate of the present invention can be used without modification as a raw material for electronic parts such as the aforementioned capacitors and PTC thermistors, but when the spherical barium titanate of the present invention is calcined, little sintering occurs, so that the particle diameter and form of the original spherical barium titanate prior to calcining is maintained. As a result, a cubic or tetragonal spherical barium titanate with high dispersibility and narrow particle size distribution is obtained.

[0092]

These spherical barium titanates have narrower particle size distribution and are more spherical relative to barium titanate obtained by conventional solid-phase methods or wet methods. Consequently, there is little air conduction during molding, so that lamination can be controlled. As a result, it is possible to obtain a uniform high-density molding, allowing great improvement in the final density of the sintered body.

[0093]

By using the aforementioned spherical barium titanate, capacitors with excellent dielectric properties and uniform particle diameter can be obtained. Moreover, by sintering the aforementioned spherical barium titanate at a high temperature, a tetragonal cuboid barium titanate with a narrow particle size distribution can be obtained.

[0094]

This tetragonal cuboid barium titanate is a tighter and higher-density barium titanate than the aforementioned spherical barium titanate, and so it is easier to exercise strict control over the particle diameter and grain boundary of the ceramic. As a result, capacitors and PTC thermistors can be obtained which have even better dielectric characteristics by using this tetragonal cuboid barium titanate.

[0095]

Moreover, by sintering spherical barium titanate containing tetragonal barium titanate having a different particle diameter, a tetragonal cuboid barium titanate with uniform particle diameter can be more readily obtained, which facilitates production of devices such as capacitors and PTC thermistors of the type described above which have excellent dielectric characteristics.

[0096]

In addition, by sintering spherical barium titanate containing particles having different compositions composed of high-sintering strontium titanate, barium zirconate or barium titanate zirconate, it is possible to carry out low-temperature sintering while also bringing about a reaction between the barium titanate and the particles having a different composition. As a result, the electrical characteristics of devices such as capacitors and PTC thermistors are additionally improved.

[0097]

Application examples

The present invention is described in additional detail below by providing application examples.

[0098]

Application Example 1

Aqueous titanium tetrachloride solution (titanium content 16.4%; manufactured by Osaka Titanium) was hydrolyzed with 5% aqueous ammonia solution, and the resulting titanium hydroxide gel was filtered and washed with water to obtain a titanium hydroxide cake (I) with a titanium oxide concentration of 12.3%, based on weight conversion by ignition loss.

[0099]

221 g of 30% aqueous hydrogen peroxide solution were added to an aqueous solution produced by uniformly dispersing 200 g titanium hydroxide cake (I) in 654 g water. The molar ratio of hydrogen peroxide with respect to titanium oxide at this time (H_2O_2/TiO_2 (molar ratio)) was 6.34. In addition, the concentration of titanium oxide in the resulting slurry was 0.312 mol/L, calculated assuming that 70% of the 30% aqueous hydrogen peroxide solution was water.

[0100]

The resulting slurry was mixed until uniform for 2 h at 60°C to obtain a suspension (II). This suspension was then allowed to cool to 40°C, and 136 g barium hydroxide•octahydrate (Ba/Ti

(molar ratio) = 1.4) were added, whereupon the temperature was increased to 100°C over 0.5 h under a nitrogen flow. A reaction was then allowed to occur for 4 h under reflux.

[0101]

The barium titanate manufactured by this reaction was a spherical aggregate constituted by primary particles with particle diameters of 0.01-0.03 μm, where the 90% numerical distribution particle diameter as determined by electron microscopy was 0.63-0.77 μm. The particle size distribution was narrow, and the average particle diameter was 0.70 μm.

[0102]

Figure 1 is an electron micrograph showing the particle structure of the barium titanate manufactured according to Application Example 1 at a magnification of 30,000x. As shown in Figure 1, the barium titanate manufactured in Application Example 1, when magnified at 30,000x, has a highly spherical particle form, and in addition, a fairly uniform particle diameter and a narrow particle size distribution.

[0103]

Application Example 2

200 g of the titanium hydroxide cake (I) produced in Application Example 1 were dispersed uniformly in 217 g water, and to this solution were added 820 g (H_2O_2/TiO_2 (molar ratio) = 10.0) of 30% aqueous hydrogen peroxide solution. A slurry was obtained having a titanium oxide concentration of 0.312 mol/L in the same manner as in Application Example 1.

[0104]

The resulting slurry was mixed uniformly for 2 h at 20°C to obtain a suspension. 136 g barium hydroxide•octahydrate (Ba/Ti (molar ratio) = 1.4) were added to this suspension, whereupon the temperature was increased from 20°C to 100°C over 0.75 h. A reaction was then allowed to occur for 4 h under reflux.

[0105]

The resulting barium titanate was a spherical aggregate constituted by primary particles with particle diameters of 0.01-0.03 μm, where the 90% numerical distribution particle diameter as determined by electron microscopy was 0.69-1.03 μm. The particle size distribution was narrow, and the average particle diameter was 0.86 μm.

[0106]

Application Example 3

200 g of the titanium hydroxide cake (I) produced in Application Example 1 were dispersed uniformly in 751 g water, and to this aqueous solution were added 82 g (H_2O_2/TiO_2 (molar ratio) = 2.35) of 30% aqueous hydrogen peroxide solution. A slurry was obtained having a titanium oxide concentration of 0.312 mol/L in the same manner as in Application Example 1.

[0107]

The resulting slurry was then mixed uniformly for 2 h at 60°C to obtain a suspension. After allowing the suspension to cool to 40°C, 136 g barium hydroxide•octahydrate (Ba/Ti (molar ratio) = 1.4) were added to this suspension, whereupon the temperature was increased to 100°C over 0.5 h under a nitrogen flow. A reaction was then allowed to occur for 4 h under reflux.

[0108]

The resulting barium titanate was a spherical aggregate constituted by primary particles with particle diameters of 0.01-0.03 μm, where the 90% numerical distribution particle diameter as determined by electron microscopy was 0.58-0.70 μm. The particle size distribution was narrow, and the average particle diameter was 0.64 μm.

[0109]

Application Example 4

200 g of the titanium hydroxide cake (I) produced in Application Example 1 were dispersed uniformly in 80 g water, and to this aqueous solution were added 221 g (H_2O_2/TiO_2 (molar ratio) = 6.35) 30% aqueous hydrogen peroxide solution. A slurry was obtained having a titanium oxide concentration of 0.75 mol/L.

[0110]

The resulting slurry was mixed uniformly for 2 h at 20°C to obtain a suspension (III). 116 g barium hydroxide•octahydrate (Ba/Ti (molar ratio) = 1.2) were added to this suspension, whereupon the temperature was increased from 20°C to 100°C over 0.75 h. A reaction was then allowed to occur for 4 h under reflux.

[0111]

The resulting barium titanate was a spherical aggregate constituted by primary particles with particle diameters of 0.01-0.03 μm, where the 90% numerical distribution particle diameter as

determined by electron microscopy was 0.27-0.43 μm. The particle size distribution was narrow, and the average particle diameter was 0.35 μm.

[0112]

Figure 2 is an electron micrograph showing the particle structure of the barium titanate manufactured according to Application Example 4 at a magnification of 30,000x. Figure 3 is an electron micrograph showing the particle structure of the barium titanate manufactured according to Application Example 4 at a magnification of 100,000x.

[0113]

The spherical barium titanate of Application Example 4 had a highly spherical particle form, even under magnification of 100,000x, and the particle diameter was nearly uniform. In addition, the particle size distribution was narrow.

[0114]

Application Example 5

194 g barium hydroxide•octahydrate (Ba/Ti (molar ratio) = 2.0) were added to the same suspension (III) as produced in Application Example 4, and a barium titanate was obtained by the same procedures in Application Example 4.

[0115]

The resulting barium titanate was a spherical aggregate constituted by primary particles with particle diameters of 0.01-0.03 μm, where the 90% numerical distribution particle diameter as determined by electron microscopy was 0.15-0.25 μm. The particle size distribution was narrow, and the average particle diameter was 0.20 μm.

[0116]

Application Example 6

111 g (H_2O_2/TiO_2 (molar ratio) = 6.35) of 30% aqueous hydrogen peroxide solution were added to an aqueous solution produced by uniform dispersion of 100 g of the titanium hydroxide cake (I) produced in Application Example 1 in 2295 g water. A slurry was obtained having a titanium oxide concentration of 0.06 mol/L.

[0117]

The resulting slurry was mixed uniformly for 2 h at 20°C to obtain a suspension. 194 g barium hydroxide•octahydrate (Ba/Ti (molar ratio) = 4.0) were added to this solution, whereupon

the temperature was increased from 20°C to 100°C over 0.75 h. A reaction was then allowed to occur for 4 h under reflux.

[0118]

The resulting barium titanate was a spherical aggregate constituted by primary particles with particle diameters of 0.01-0.03 μm, and the 90% numerical distribution particle diameter as determined by electron microscopy was 0.45-0.83 μm. The particle size distribution was narrow, and the average particle diameter was 0.64 μm.

[0119]

Application Example 7

136 g barium hydroxide•octahydrate (Ba/Ti (molar ratio) = 1.4) were added to the same suspension (II) as produced in Application Example 1 at 20°C, and the temperature was increased to 60°C over 0.25 h. After then allowing a three-hour aging reaction to occur at 60°C, the temperature was increased to 100°C over 0.5 h, and a reaction was carried out for 4 h under reflux at 100°C.

[0120]

The resulting barium titanate was a spherical aggregate constituted by primary particles with particle diameters of 0.01-0.03 μm, where the 90% numerical distribution particle diameter as determined by electron microscopy was 0.63-0.77 μm. The particle size distribution was narrow, and the average particle diameter was 0.70 μm.

[0121]

Application Example 8

136 g barium hydroxide•octahydrate (Ba/Ti (molar ratio) = 1.4) were added to the same suspension (II) as produced in Application Example 1 at 20°C, and the temperature was increased to 80°C over 0.5 h. After then allowing a three-hour aging reaction to occur at 80°C, the temperature was increased to 100°C over the course of 0.25 h. A 4-h reaction was then allowed to occur under reflux at 100°C.

[0122]

The resulting barium titanate was a spherical aggregate constituted by primary particles with particle diameters of 0.01-0.03 μm, where the 90% numerical distribution particle diameter as determined by electron microscopy was 1.22-1.82 μm. The particle size distribution was narrow, and the average particle diameter was 1.52 μm.

[0123]

Application Example 9

96 g barium hydroxide•octahydrate (Ba/Ti (molar ratio) = 0.99) were added at 20°C to the same suspension (II) as produced in Application Example 1, the temperature was then increased to 80°C over 0.5 h, and an aging reaction was allowed to occur for 3 h at 80°C. Subsequently, 42 g barium hydroxide•octahydrate (Ba/Ti (molar ratio) = 0.41) were added and the temperature was increased from 80°C to 100°C over 0.25 h, whereupon a reaction was carried out for 6 h under reflux at 100°C. The total amount of added barium hydroxide•octahydrate was 138 g, which corresponded to a molar ratio of barium with respect to titanium (Ba/Ti (molar ratio)) of 1.4.

[0124]

The resulting barium titanate was a spherical aggregate constituted by primary particles with particle diameters of 0.03-0.1 μm, where the 90% numerical distribution particle diameter as determined by electron microscopy was 0.34-0.62 μm. The particle size distribution was narrow, and the average particle diameter was 0.48 μm.

[0125]

Application Example 10

The same suspension (II) as produced in Application Example 1 was allowed to cool to 40°C, whereupon 87 g barium hydroxide•octahydrate (Ba/Ti (molar ratio) = 0.9) were added. The temperature was then increased to 80°C over 0.5 h under a flow of nitrogen, and an aging reaction was allowed to occur for 2 h. Subsequently, 49 g barium hydroxide•octahydrate (Ba/Ti (molar ratio) = 0.5) were added and the temperature was immediately increased to 100°C, whereupon a reaction was carried out for 4 h under reflux.

[0126]

The resulting barium titanate was a spherical aggregate constituted by primary particles with particle diameters of 0.03-0.1 μm, and the 90% numerical distribution particle diameter as determined by electron microscopy was 0.63-0.77 μm. The particle size distribution was narrow, and the average particle diameter was 0.70 μm.

[0127]

Comparative Example 1

200 g of the titanium hydroxide cake (I) produced in Application Example 1 were dispersed uniformly in 809 g water, and the titanium oxide concentration was adjusted to

0.312 mol/L. 136 g barium hydroxide•octahydrate (Ba/Ti (molar ratio) = 1.4) were then added to this solution at 20°C, the temperature was increased to 60°C over a period of 0.25 h under a flow of nitrogen, and an aging reaction was carried out for 3 h at 60°C. The temperature was then increased to 100°C over 0.25 h, and a reaction was carried out for 4 h while refluxing at 100°C.

[0128]

The barium titanate obtained in this manner was a spherical aggregate constituted by primary particles with particle diameters of 0.01-0.03 μm, and the 90% numerical distribution particle diameter as determined by electron microscopy was 0.14-0.42 μm. Although the average particle diameter was 0.28 μm, the particle diameters were not uniform, and the general form was far from spherical.

[0129]

Figure 4 is an electron micrograph showing the particle structure of the barium titanate manufactured according to Comparative Example 1 at a magnification of 30,000x. As shown in Figure 4, the barium titanate manufactured according to Comparative Example 1 did not have a uniform particle diameter, and the form was not even close to spherical.

[0130]

Comparative Example 2

200 g of the titanium hydroxide cake (I) produced in Application Example 1 were dispersed uniformly in 809 g water, and the concentration of titanium oxide was adjusted to 0.312 mol/L.

[0131]

136 g barium hydroxide•octahydrate (Ba/Ti (molar ratio) = 1.4) were added to this solution at 20°C, and the temperature was increased to 100°C over a period of 0.5 h under a flow of nitrogen. A reaction was then allowed to occur for 4 h while refluxing at 100°C.

[0132]

The resulting barium titanate obtained in this manner was a spherical aggregate constituted by primary particles with particle diameters of 0.01-0.03 μm, where the 90% numerical distribution particle diameter as determined by electron microscopy was 0.08-0.16 μm. Although the average particle diameter was 0.12 μm, the general form was far from spherical.

[0133]

Application Example 11

136 g barium hydroxide•octahydrate (Ba/Ti (molar ratio) = 1.4) were added at 20°C to the same suspension (II) as produced in Application Example 1, and the temperature was increased to 100°C over a period of 0.75 h. After then allowing an aging reaction to occur for 4 h at 100°C, the content was introduced into a sealed container, and the temperature was increased to 180°C over a period of 1 h under pressurization, whereupon a reaction was allowed to occur for 4 h.

[0134]

The resulting barium titanate was a spherical aggregate constituted by primary particles with particle diameters of 0.05-0.1 μm, where the 90% numerical distribution particle diameter as determined by electron microscopy was 0.63-0.77 μm. The particle size distribution was narrow, and the average particle diameter was 0.70 μm. In addition, the aggregate was extremely dense.

[0135]

Application Example 12

136 g of barium hydroxide•octahydrate (Ba/Ti (molar ratio) = 1.4) were added at 20°C to the same suspension (II) as produced in Application Example 1, and the temperature was increased to 100°C over 0.75 h. Subsequently a reaction was allowed to occur for 4 h at 100°C.

[0136]

The resulting barium titanate was filtered and washed with water, followed by slurrification with 1000 g water. 200 g barium hydroxide•octahydrate were then added and mixed with this slurry, and the material was introduced into a sealed container. The temperature was then increased to 180°C over a period of 1 h, and a reaction was allowed to occur for 4 h at 180°C.

[0137]

The resulting barium titanate was a spherical aggregate constituted by primary particles with particle diameters of 0.05-0.1 μm, where the 90% numerical distribution particle diameter was 0.63-0.77 μm, as determined by electron microscopy. The particle size distribution was narrow, and the average particle diameter was 0.70 μm.

[0138]

Application Example 13

4000 g water and 410 g urea were added to 500 g aqueous titanium tetrachloride solution (titanium content 16.4%), whereupon the temperature was increased and a decomposition reaction

was allowed to occur for 4 h under reflux. A slurry of microparticulate hydrated titanium oxide having an anatase structure was obtained.

[0139]

The resulting slurry was filtered and washed with water to obtain an anatase-type hydrated titanium hydroxide cake with a titanium oxide concentration of 21.0% calculated by weight conversion based on ignition loss.

[0140]

200 g of this anatase-type hydrated titanium hydroxide cake were niformly dispersed in 1228 g water, and 420 g of 30% aqueous hydrogen peroxide solution (H_2O_2/TiO_2 (molar ratio = 7.06)) were added to this solution. The concentration of titanium oxide in the resulting slurry was calculated at 0.312 mol/L assuming that 70% of the 30% aqueous hydrogen peroxide solution was water.

[0141]

The resulting slurry was mixed uniformly over 2 h at 60°C to obtain a suspension, 231.9 g barium hydroxide•octahydrate (Ba/Ti (molar ratio) = 1.4) were added to the suspension, and a reaction was carried out for 6 h under reflux at 100°C.

[0142]

The resulting barium titanate was a spherical aggregate constituted by primary particles with particle diameters of 0.01-0.03 μm, and the 90% numerical distribution particle diameter as determined by electron microscopy was 0.63-0.77 μm. The particle size distribution was narrow, and the average particle diameter was 0.70 μm.

[0143]

Application Example 14

3904 g water and 137 g 30% hydrogen peroxide (H_2O_2/TiO_2 (molar ratio) = 2.35) were added to 500 g aqueous titanium tetrachloride solution (titanium content 16.4%), and after mixing uniformly for 2 h, hydrolysis was carried out using an aqueous ammonia solution. The resulting titanium hydroxide was filtered and washed to obtain titanium hydroxide cake (yellow) with a titanium oxide concentration of 13.0% calculated by weight conversion based on ignition loss.

[0144]

200 g of this titanium hydroxide cake were uniformly dispersed in 836 g water, and 43 g of 30% aqueous hydrogen peroxide solution (H_2O_2/TiO_2 (molar ratio = 1.18)) were added to the solution. The concentration of titanium oxide in the resulting slurry was calculated at 0.312 mol/L.

[0145]

The resulting slurry was mixed uniformly over 2 h at 60°C to obtain a suspension, 143.5 g barium hydroxide•octahydrate (Ba/Ti (molar ratio) = 1.4) were added to the suspension, whereupon the reaction was carried out at 100°C.

[0146]

The resulting barium titanate was a spherical aggregate constituted by primary particles with particle diameters of 0.01-0.03 μm, where the 90% numerical distribution particle diameter as determined by electron microscopy was 0.63-0.77 μm. The particle size distribution was narrow, and the average particle diameter was 0.70 μm.

[0147]

Application Example 15

1000 g distilled water were gradually added dropwise to 102.4 g titanium isopropoxide, and hydrolysis was allowed to occur. 172 g of 30% hydrogen peroxide (H_2O_2/TiO_2 (molar ratio) = 7.06) were then added to produce a titanium oxide concentration of 0.312 mol/L. This aqueous solution was then heated to 60°C and stirred for 2 h to obtain a suspension.

[0148]

159 g barium hydroxide•octahydrate (Ba/Ti (molar ratio) = 1.4) were then gradually added to the resulting suspension solution at 20°C, and the temperature was increased from 20°C to 100°C over a period of 0.75 h, followed by refluxing for 4 h.

[0149]

The resulting barium titanate was a spherical aggregate constituted by primary particles with particle diameters of 0.01-0.03 μm, where the 90% numerical distribution particle diameter as determined by electron microscopy was 0.44-0.60 μm. The particle size distribution was narrow, and the average particle diameter was 0.52 μm.

[0150]

Application Example 16

Spherical barium titanate with an average particle diameter of 0.70 μm obtained in Application Example 1 was washed with 3000 g water, and after slurrification in 1500 g water, the slurry was heated to 60°C over a period of 1 h. 10 mL acetic acid were then added to adjust the pH to 8.50, and after stirring for 1 h at 60°C, the slurry was filtered, washed with 3000 g of water and dried.

[0151]

The results of this treatment gave a 1.005 molar ratio of barium with respect to titanium. The molar ratio was a value determined by fluorescent X-ray analysis, and the molar ratio of barium with respect to titanium in the calcined powders below was also determined by fluorescent X-ray measurements.

[0152]

The resulting barium titanate powder was milled for 1 h with a pulverizer, and was then calcined at 1000°C.

[0153]

The barium titanate obtained by the aforementioned calcining was a dense and unsintered tetragonal cuboid barium titanate with a 90% numerical distribution particle diameter of 0.49-0.91 μm, as determined by electron microscopy. The average particle diameter was 0.70 μm.

[0154]

Application Example 17

100 g of the spherical barium titanate obtained in Application Example 1 was filtered, dried and slurrified in 1000 g water. The temperature was increased to 60°C, and then 5 mL acetic acid were added to adjust the pH to 8.80, whereupon an aging reaction was allowed to occur for 1 h at 60°C. Subsequently, the material was filtered and washed with 1000 g of water, followed by drying. This treatment resulted in the production of a barium molar ratio of 1.018 with respect to titanium in the barium titanate.

[0155]

The resulting powder was heated steadily for 3 h from 20°C to 1100°C, and was calcined for 2 h at 1100°C, whereupon the material was steadily cooled to 20°C over 3 h.

[0156]

The barium titanate obtained as a result of the above calcining was an unsintered tetragonal cuboid barium titanate with a 90% numerical distribution particle diameter of 0.49-0.91 μm and an average particle diameter of 0.70 μm, as determined by electron microscopy.

[0157]

Figure 5 is an electron micrograph showing the particle structure of the tetragonal cuboid barium titanate manufactured in Application Example 17 at a magnification of 10,000x. Figure 6 is an electron micrograph showing the tetragonal cuboid barium titanate manufactured in Application Example 17 at a magnification of 20,000x. As shown in Figures 5 and 6, the tetragonal cuboid barium titanate manufactured in Application Example 17 had a cuboid form, and the particle diameters were fairly uniform.

[0158]

<u>Application Example 18</u>

After adding yttrium nitrate to aqueous titanium tetrachloride solution at an yttrium content of 1% with respect to the weight of the titanium content, hydrolysis was carried out with aqueous ammonia solution. The resulting yttrium-containing titanium hydroxide gel was filtered and washed with water to obtain an yttrium-containing titanium hydroxide cake with a titanium oxide concentration of 12.3% calculated by weight conversion based on ignition loss.

[0159]

200 g of the resulting yttrium-containing titanium hydroxide cake were dispersed uniformly in 654 g water, and to this aqueous solution were added 221 g of 30% aqueous hydrogen peroxide solution (H_2O_2/TiO_2 (molar ratio = 6.35)). A reaction was then carried out in the same manner as in Application Example 1.

[0160]

The resulting barium titanate was a spherical aggregate constituted by primary particles with particle diameters of 0.01-0.03 μm, where the 90% numerical distribution particle diameter was 0.63-0.94 μm as determined by electron microscopy. The particle size distribution was narrow, and the average particle diameter was 0.78 μm.

[0161]

Application Example 19

200 g of the titanium hydroxide cake (I) produced in Application Example 1 were dispersed uniformly in 600 g water and 54 g isopropyl alcohol, whereupon 221 g of 30% aqueous hydrogen peroxide solution (H_2O_2/TiO_2 (molar ratio) = 6.35) were added, and a reaction was subsequently allowed to occur in the same manner as in Application Example 1.

[0162]

The resulting barium titanate was a spherical aggregate constituted by primary particles with particle diameters of 0.01-0.03 μm, where the 90% numerical distribution particle diameter was 0.50-0.74 μm, as determined by electron microscopy. The particle size distribution was narrow, and the average particle diameter was 0.62 μm.

[0163]

Application Example 20

Spherical barium titanate with an average particle size of 0-95 μm and a 90% numerical distribution particle diameter of 0.85-1.05 μm, as determined by electron microscopy, which was obtained using hydrogen peroxide according to the present invention, was filtered and dried. The temperature was then increased from 20°C to 1000°C at a constant rate over a period of 3 h. After calcining for 2 h at 800°C, the temperature was then decreased to 20°C over a period of 3 h.

[0164]

The unsintered barium titanate obtained by the calcining process described above was a cubic spherical barium titanate with an average particle diameter of 0.95 μm, and thus maintained the particle diameter of the material prior to calcining. This cubic spherical barium titanate also had a narrow particle size distribution and excellent dispersion properties.

[0165]

Figure 7 is an electron micrograph showing the particle structure of the cubic spherical barium titanate manufactured according to Application Example 20 at a magnification of 30,000x. The cubic spherical barium titanate of Application Example 20, as shown in Figure 7, has a highly spherical particle form and fairly uniform particle diameter, even when magnified at 30,000x.

[0166]

Application Example 21

233 g of 30% aqueous hydrogen peroxide solution (H_2O_2/TiO_2 (molar ratio) = 3.00) and 600 g water were added to 200 g aqueous titanium tetrachloride solution (titanium content 16.4%), and after mixing, 80 g of tetragonal barium titanate with an average particle diameter of 0.2 μm were added. Stirring and mixing were carried out for 3 h.

[0167]

Next, 144 g urea were added, and after increasing the temperature from 20 to 100°C at a constant rate over a period of 0.5 h, a thermal hydrolysis reaction was allowed to occur by refluxing for 4 h at 100°C.

[0168]

After the reaction, filtration and water rinsing of the slurry were repeatedly carried out, and 1200 g water were added to the resulting titanium hydroxide cake containing barium titanate. 302 g barium hydroxide•octahydrate (Ba/Ti (molar ratio) = 1.4) were then added to the slurry, and an aging reaction was carried out for 2 h at 50°C under a flow of nitrogen. A reaction was then allowed to occur for 4 h under reflux at 100°C.

[0169]

Other than the tetragonal barium titanate contained on the interior, the resulting barium titanate was a spherical aggregate constituted by primary particles with particle diameters of 0.03-0.1 μm, where the aggregates had superior crystallinity, with a 90% numerical distribution particle diameter of 0.20-0.36 μm as determined by electron microscopy. In addition, the particle size distribution was narrow, and the average particle diameter was 0.28 μm.

[0170]

Figure 8 is an electron micrograph showing the particle structure of the spherical barium titanate manufactured according to Application Example 21 at a magnification of 50,000x. The spherical barium titanate manufactured in Application Example 21, as shown in Figure 8, had a highly spherical particle form and fairly uniform particle diameter, even when magnified at 50,000x. In addition, the particle size distribution was narrow.

[0171]

Application Example 22

600 g water were added to 200 g aqueous titanium tetrachloride solution (titanium content 16.4%), and after mixing for 1 h until uniform, 80 g tetragonal barium titanate with an average particle diameter of 0.8 μm were added. Stirring and mixing were then carried out for 3 h.

[0172]

Next, 5% aqueous ammonia solution was added gradually to adjust the pH to 7, and subsequently, filtration and water rinsing were repeatedly carried out. 1000 g water were then added to the resulting titanium hydroxide cake containing barium titanate, and after stirring, 200 g of 30% hydrogen peroxide (H_2O_2/TiO_2 (molar ratio) = 2.58) were added, and the mixture was stirred for 2 h at 60°C.

[0173]

The resulting slurry was then cooled to 20°C, and 302 g barium hydroxide•octahydrate (Ba/Ti (molar ratio) = 1.4) were added, whereupon an aging reaction was allowed to occur for 2 h at 60°C under a flow of nitrogen. A reaction was then allowed to occur for 4 h under reflux at 100°C.

[0174]

Other than the tetragonal barium titanate contained on the interior, the resulting barium titanate was a spherical aggregate constituted by primary particles with particle diameters of 0.03-0.1 μm, where the aggregates had superior crystallinity, with a 90% numerical distribution particle diameter of 0.78-1.06 μm as determined by electron microscopy. In addition, the particle size distribution was narrow, and the average particle diameter was 0.92 μm.

[0175]

Comparative Example 3

136 g barium hydroxide•octahydrate (Ba/Ti (molar ratio) = 1.4) were added at 20°C to the same suspension (II) as produced in Application Example 1, and the temperature was increased to 180°C at a constant rate over a period of 0.75 h in a sealed container. Subsequently a reaction was allowed to occur for 4 h at 180°C. The resulting barium titanate was a microparticulate with particle diameters of 0.02-0.1 μm.

[0176]

Application Example 23

600 g water was added to 200 g aqueous titanium tetrachloride solution (titanium content = 16.4%), and after mixing for 1 h until uniform, 80 g barium zirconate with an average particle diameter of 0.8 μm manufactured by a solid-phase method were added. Stirring and mixing were carried out for 3 h.

[0177]

Next, 5% aqueous ammonia solution was added gradually to adjust the pH to 7, and subsequently, filtration and water rinsing were repeatedly carried out. 1000 g water were then added to the resulting titanium hydroxide cake containing barium zirconate, and after stirring, 200 g of 30% hydrogen peroxide (H_2O_2/TiO_2 (molar ratio) = 2.58) were added, and the mixture was stirred for 2 h at 60°C.

[0178]

The resulting slurry was then cooled to 20°C, and 302 g barium hydroxide•octahydrate (Ba/Ti (molar ratio) = 1.4) were added, whereupon an aging reaction was allowed to occur for 2 h at 60°C under a flow of nitrogen. A reaction was then allowed to occur for 4 h under reflux at 100°C.

[0179]

Other than the barium zirconate contained on the interior, the resulting barium zirconate was a spherical aggregate constituted by primary particles with particle diameters of 0.03-0.1 μm, where the aggregates had superior crystallinity, with a 90% numerical distribution particle diameter of 0.78-1.06 μm as determined by electron microscopy. In addition, the particle size distribution was narrow, and the average particle diameter was 0.92 μm.

[0180]

Comparative Example 4

Commercially-available barium titanate manufactured by a wet method was observed under an electron microscope. The material was composed of non-uniform particles with an average particle diameter of 0.1 μm and a high level of sintering. Cavitated particles were observed.

[0181]

Figure 9 is an electron micrograph presenting the particle structure of the barium titanate of Comparative Example 4 at a magnification of 100,000. As shown in Figure 9, the barium titanate of Comparative Example 4 had a high level of sintering, and the particle shape was not uniform.

[0182]

Comparative Example 5

Commercially-available barium titanate manufactured by a solid phase method was observed under an electron microscope. The material was composed of tetragonal barium titanate with an average particle diameter of 0.8 μm and significant sintering. However, the shape was indeterminate, and the particles had a wide particle size distribution.

[0183]

Figure 10 is an electron micrograph that presents the particle structure of the barium titanate of Comparative Example 5 at a magnification of 10,000. Figure 10 was compared with Figure 5 (where Figure 5 is an electron micrograph presenting the particle structure of tetragonal cuboid barium titanate manufactured in Application Example 17 of the present invention at a magnification of 10,000), and it was found that superior characteristics in regard to shape, particle size distribution and sintering were present in the tetragonal cubic barium titanate manufactured in Application Example 17 of the present invention, relative to the commercially-available tetragonal barium titanate manufactured by the solid phase method.

Brief description of the figures

Figure 1 is an electron micrograph presenting the particle structure of the spherical barium titanate manufactured in Application Example 1 at a magnification of 30,000x.

Figure 2 is an electron micrograph presenting the particle structure of the spherical barium titanate manufactured in Application Example 4 at a magnification of 30,000x.

Figure 3 is an electron micrograph presenting the particle structure of the spherical barium titanate manufactured in Application Example 4 at a magnification of 100,000x.

Figure 4 is an electron micrograph presenting the particle structure of the spherical barium titanate manufactured in Comparative Example 1 at a magnification of 30,000x.

Figure 5 is an electron micrograph presenting the particle structure of the tetragonal cuboid barium titanate manufactured in Application Example 17 at a magnification of 10,000x.

Figure 6 is an electron micrograph presenting the particle structure of the tetragonal cuboid barium titanate manufactured in Application Example 17 at a magnification of 20,000x.

Figure 7 is an electron micrograph presenting the particle structure of the cubic spheroid barium titanate manufactured in Application Example 20 at a magnification of 30,000x.

Figure 8 is an electron micrograph presenting the particle structure of the spherical barium titanate manufactured in Application Example 21 at a magnification of 50,000x.

Figure 9 is an electron micrograph presenting the particle structure of the commercially-available barium titanate manufactured by a wet method in Comparative Example 4 at a magnification of 100,000x.

Figure 10 is an electron micrograph presenting the particle structure of the commercially-available tetragonal barium titanate manufactured by the solid phase method of Comparative Example 5 at a magnification of 10,000x.

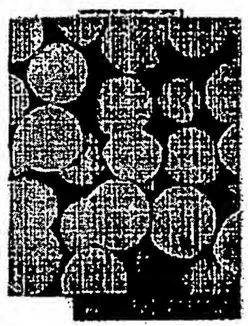


Figure 1. Photograph substituted for figure (color)

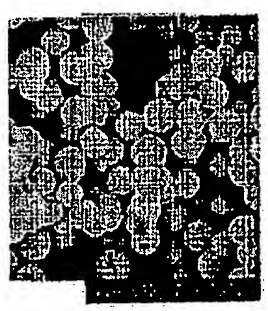
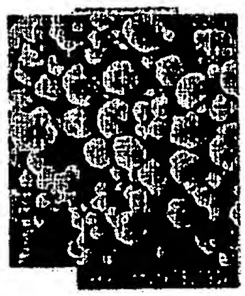


Figure 2. Photograph substituted for figure (color)

Figure 3. Photograph substituted for figure (color)



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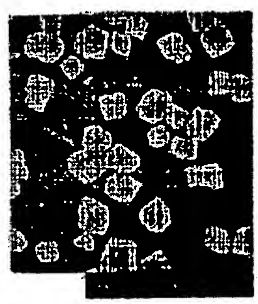

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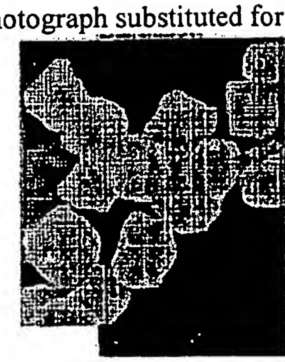

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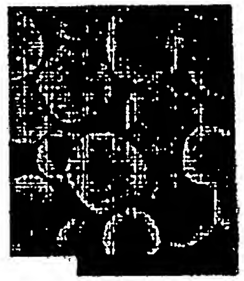

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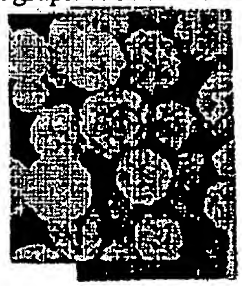

Figure 8. Photograph substituted for figure (color)

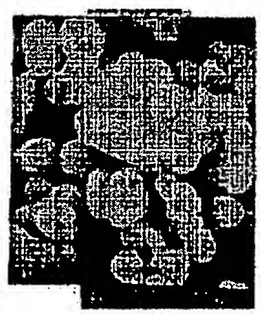

Figure 9. Photograph substituted for figure (color)

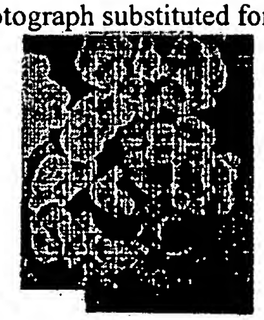

Figure 10. Photograph substituted for figure (color)